(12) **EUROPEAN PATENT APPLICATION**

(54) Sealed storage battery and method for making its electrode.

(57) A sealed storage battery comprises a positive electrode (11) including a metallic oxide as an active material, a negative electrode (10) including hydrogen-occlusion-alloy powder (4) capable of charging and discharging electrochemically hydrogen as an active material, an alkaline electrolyte, and a separator (12) for absorbing and holding the alkaline electrolyte. The hydrogen-occlusion-alloy powder (4) has a crystal structure of $CaCu_5$ type, is provided with numerous irregularities on the surface thereof, and has SF-value of 2.5 or below, which SF-value represents a plateau characteristic of equilibrium pressure of hydrogen releasing. The numerous irregularities on the surface of the alloy powder (4) causes oxygen being generated from the positive electrode (11) to be eliminated promptly.

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FIG. 3

FIG. 5

_____4

_____5

_____6

SAFTY VALVE

POSITIVE TERMINAL(+)

POSITIVE LEAD

SEALING PLATE

INSULATING GASKET

INSULATOR

SEPARATOR MEANS

CASE(-)

INSULATOR

POSITIVE ELECTRODE 11

NEGATIVE ELECTRODE 10

SEPARATOR 12

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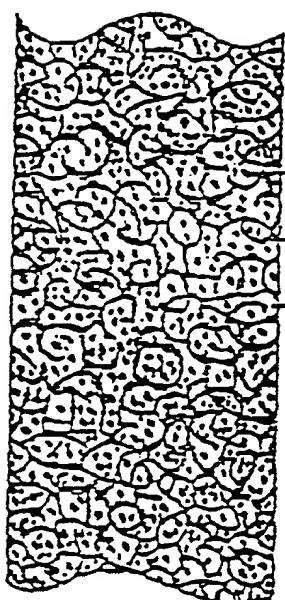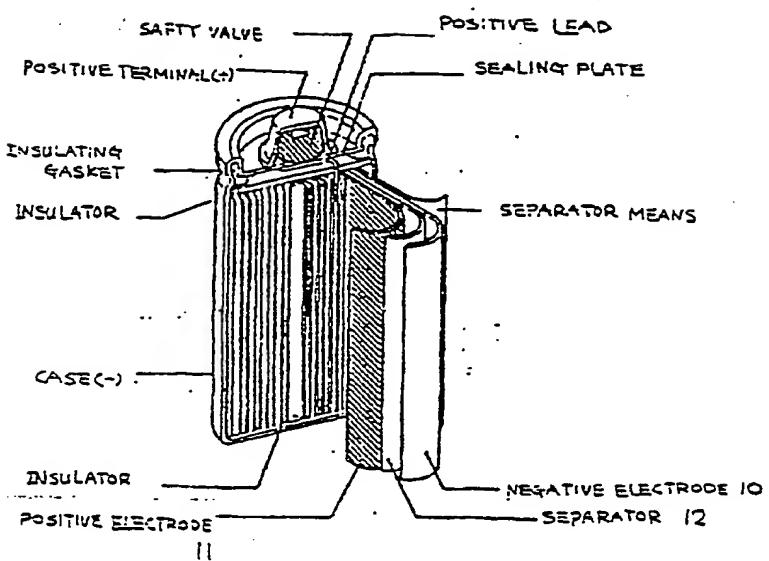
TITLE OF THE INVENTION

SEALED STORAGE BATTERY AND METHOD FOR MAKING ITS ELECTRODE

BACKGROUND OF THE INVENTION

This invention relates to a sealed storage battery

5   and a method for making its electrode, and more

particularly, the present invention relates to an alkaline

storage battery.

Nowadays, a lead-acid storage battery and a

nickel-cadmium storage battery are predominantly used as a

10 sealed secondary battery. Although the lead-acid storage

battery is of low cost, this battery is insufficient from

the point of the view of weight density or cycling

life-time in the case of being used as electric power

supply of a portable apparatus which is used for a long

15 time. On the other hand, although the nickel-cadmium

storage battery is of comparatively high cost, the demand

for this battery extremely increases, and more

particularly, this battery has become widely applied to the

field where high reliability is required because this

20 battery can remove the drawbacks of the lead-acid storage

battery. Various improvements for providing with high

capacitance have been made since it is desired for this

nickel-cadmium storage battery to have higher energy

density electric power supply of the portable apparatus in

25 addition to the special merits described above. However, a

cadmium electrode as the negative electrode has the high utilization factor of an active material, especially large electrode decrease at a high-rate discharge in comparison with a nickel electrode as the positive electrode.

5 Moreover, in the case of constructing the storage battery of capacitance regulation at the positive electrode, it is necessary to take allowance except capacitance at the positive electrode so as to generate no hydrogen at the negative electrode when overcharging. Therefore, the

10 negative electrode has the capacitance capable of charge and discharge larger than the positive electrode. Moreover, it is necessary for the porosity of he negative electrode to be increased to an optimum value in order that an overcharge, oxygen gas generated from the positive

15 electrode is efficiently absorbed by the negative electrode. However, it is not attainable for the negative electrode to have higher energy density until a rapid improvement is made. Therefore, there is a limit in the improvement of the energy density of the nickel-cadmium

20 storage battery.

Recently, a metallic oxide-hydrogen storage battery has attracted the attention of many people in which battery a hydrogen-occlusion-alloy that can occlude and release electrochemically hydrogen is applied as the material of

25 the negative electrode, in stead of the nickel-cadmium

storage battery. In this storage battery, even if hydrogen
is generated from the negative electrode on overcharge,
hydrogen is diddipated through discharge or is occluded by
the hydrogen-occlusion-alloy of the negative electrode, in
5 so far as hydrogen is not released out of the battery.
Moreover, this storage battery has a higher energy density
per unit volume than the nickel-cadmium storage battery.
As a result, in the case that the capacity of this storage
battery is equal to that of the nickel-cadmium storage
10 battery, this storage battery can be constructed such that
the volume of the negative electrode of this storage
battery is smaller than that of the cadmium negative
elecrode. Therefore, a larger active material as the
positive electrode can be appropriated in the residual
15 space of this storage battery, so that a higher energy
density is expected. Moreover, the material of the
hydrogen-occlusion-alloy obviates the need for a metallic
cadmium which is a main component of the cadmium electrode,
so that there is little pollution by heavy metal or the
20 like.

   With these points as background, the as a new
secondary battery is developed in various fields. However,
many problems need to be solved if this storage battery is
commercialized. One of the important problems is that
25

techniques for constructing a sealed storage battery by means of a simple method and for lengthen the life-time of the battery are completed like the nickel-cadmium storage battery which is practically applied nowadays. Namely,

5 metallic ocide-hydrogen storage battery, whose maintenance is easy and which has high reliability, must be performed. From the above-mentioned stand point, as the condition which is required to the hydrogen-occlusion-electrode using the hydrogen-occlusion-alloy, the

10 hydrogen-occlusion-electrode must have a stability in alkaline electrolyte and occlude and release electrochemically hydrogen. Moreover, more important conditions are following conditions (1)-(3).

(1) The hydrogen-occlusion-electrode has a large

15 capacity for occluding and releasing electrochemically hydrogen, and discharge capacitance does not decrease even if charge and discharge are repeated.

(2) An ordinary sealed storage battery is designed such that for safety, the pressure gas in the battery is

20 kept at a given value or below with a safty valve being operated, when the pressure in the battery becomes 10 to 15 kg/cm^2. Threfore, the material must be selected which does not generate hydrogen on charging within given temperatures range where the battery is used since in this storage

25 battery system, it is necessary to be designed as well as the ordinary sealed storage battery as described above.

(3) The hydrogen-occlusion-electrode must have a corrosion resistance to oxigen generated from the positive electrode on overcharging. Moreover, the alloy material must be used which has a function carrying out smoothly oxigen-elimination reaction that on the surface of the alloy, the reaction of oxigen with hydrogen occluded gives water. Moreover, it is possible for the alloy material to construct the electrode. Although many alloy materials or many methods for constructing the electrode satisfying these conditions (1) to (3) have been contribed, these trials cannot reach the level of the properties of the sealed nickel-cadmium storage battery, i,e, the cycling life-time is 500 cycles or above, and the inner pressure of the battery is 5 to 10 kg/cm^2 or below when the battery is charged to the level of approximately 1/3 CmA.

Concernig (1), an alloy of AB5, which is basic form of $CaCu_5$ type alloy and in which lantharum series metals are mainly used as A and nickel is mainly used as B, has the largest possibility of a practical application noeadays. However, even if the alloy of AB_5 is used as a hydrogen-occlusion-elecrode, the electrode is oxidized by oxigen gas generated at the positive electrode on overcharge to decrease the capacity of occluding and releasing hydrogen. In order to solve the above-mentioned problem, the method that the surface of the alloy is

covered with a metal having the property of corrosion resistance (Japanese patent provisional publication No.61-64069 or No. 61-101957) and the method that entire electrode is covered with the same metals described above

5   (Japanese patent provisional publication No. 60-77357) are proposed. These methods shows some effects. However, large amount of covering metal are needed when occluding and releasing hydrogen constantly for a long time. Therefore, this fact causes the hydrogen-occlusion-alloy to

10   be small in quantity relatively. As a result, capacitance density per unit volume decreases, so that this is disadvantage in making the battery having high capacitance.

Concerning (2), it is necessary to guarantee the safty of the battery when seeing from a standpoint of user.

15   Therefore, it is necessary to provide with a safty valve which releases the gas generated in the battery out of the battery when inner pressure rises above a given value, in order that the battery does not be damaged and does not explode in case of the abnormal increment of the inner

20   pressure. However, the actuation of the safty valve causes the electrolyte to release out of the battery, so that the reduction of the electrolyte allows the batery property to deteriorate. Therefore, it is an effectual method for the improvement of the battery property, especially cycling

25   life-time to avoid the increment of the inner pressure. As

a result, the materials which does not generate hydrogen on
charging have been selected by using the materials having a
low equilibrium pressure of hydrogen (Japanes patent
provisional publication No. 59-181459 or No. 61-47075).

5   Concerning (3), various methods have been proposed
that oxygen gas generated when overcharging is reacted
effectually so as to decrease the inner pressure of the
battery. As described above, the increment of the inner
pressure by the generation of oxygen gas is one of the

10   reasons for actuating the safety valve. Therefore, it is
necessary to change oxygen generated to water rapidly so as
to prevent the increment of the inner pressure of the
battery. Moreover, there is another important problem that
alloy is oxidized by oxygen gas generated. Hydrogen is

15   occluded in the inner portion of the alloy and an
electrical potential itself does not carry out oxidation.
However, when repeating charge and discharge, oxidation
progresses gradually from the surface of the alloy, which
surface is contact with oxygen, to the inner portion of the

20   alloy. As a result, an electron conduction property
decreases. Moreover, the amount of hydrogen to be
occluded and to be released decreases, and the decrease of
a discharge voltage and the decrease of the property of the
cycling life-time arise. It is necessary to make the

25   electrode having an excellent corrosion resistance in order

to avoid the above-mentioned problems. However, nowadays, the sealed metallic oxide-hydrogen storage battery cannot be obtained which solves above-mentioned problems (1) to (3) and has high capacitance and long life-time. Moreover,

5   it is well known that in the sealed nickel-hydrogen storage battery, self-discharge is large. The improvement of the self-discharge must be done in order that this battery is practically applied. Therefore, the self-discharge of this battery must be improved at least to the level of the

10 sealed nickel-cadmium storage battery which is generally said that the self-discharge is large.

Nowadays, when applied to an ordinary use, a nonwoven fabric made of a polyamide is utilized as a separator of the sealed nickel-cadmium storage battery.

15 Moreover, a separator that surfactants are added to the nonwoven fabric of a polyolefin so as to improve the hydrophilic property is used for some batteries to be applied to high temperature survice. When the nonwoven fabric made of the polyamide is applied as the separator to

20 the sealed nickel-hydrogen storage battery, self-discharge arises extremely. This is because the surface of the negative electrode has a very large activity and strong reducing power in comparison with the cadmium electrode. Another reason is that polyamide is decomposed by charging

25 and discharging, the resulting oxidants and reductants in

the ionic state or polar ion coexist in the electrolyte, and then, the action that the materials reduced at the negative electrode are oxidized at the positive electrode is repeated, i.e. NO_3^- and NO_2^-, so that the self-discharge increases. When the separator is used in which separator surfactants are added to the nonwoven fabric of the polyolefin, charge and discharge cause the property of the surfactants to change so that the battery property is harmfully affected with the hydrophilic property being decreased. Therefore, the separator is required which is chemically stable to charge or discharge, and has a strong hydrophilic property to the electrolyte.

SUMMARY OF THE INVENTION

The present invention has been developed in order to remove the above-described drawbacks and contemplates to provide a sealed storage battery having a high capacitance and a long life-time by improving a hydrogen-occlusion-alloy as a negative electrode and an electrode using this alloy in order to construct a sealed metallic oxide-hydrogen storage battery.

A hydrogen-occlusion-alloy is utilized as a material of a negative electrode, and more particularly, an alloy of AB_5 having a cristal structure of CaC_5 type is utilized. Moreover, B in the alloy of AB_5 is partially replaced by

metals except nickel so as to obtain the material having
equilibrium dissocation pressure where hydrogen is occluded
and released sufficiently in the temperature range of the
battery operation. Although A in the alloy of AB_5, i.e.

5   lanthanium series metals, is gradually oxidized to change
an oxide or hydroxide by repeating charge and discharge in
a sealed storage battery system, it is difficult to prevent
basically such a phenomenon. Therefore, it is very
important to supress oxidizing velocity.

10   In the present invention, corrosion resistance can
be risen by the method that the crystallinity of the alloy
is improved. Generally, the pluralization of the alloy of
AB_5 type causes the cristallinity to decrease. However, it
is inevitable to pluralize the alloy because the alloy must

15 have dissocation pressure of hydrogen described above.
Therefore, in the present invention, the cristallinity of
the alloy is improved by the method that the puralized
alloy is rapidly cooled, treated with heat, and so on.
SF(slope factor) -value is adopted as the standard of the

20 cristallinity.

      Moreover, the increment of a specific surface area ,
namely, numerous irregularities are provided on the surface
of the alloy in order that the reducing reaction of oxygen
is promptly carried out and corrosion resistance is

25 increased only in the vicinity of the surface of the

hydrogen-occlusion-alloy.

SF-value will be described hereinbelow:

This value shows the plateau characteristic of the hydrogen-occlusion-alloy. When hydrogen is occluded or

5 released by gas reaction at a given temperature, the relation between the pressure of hydrogen and hydrogen concentration in the alloy is shown as Fig. 1. Using the pressure of hydrogen ($P_{H/M=0.75}$) when occluding hydrogen of 75 % and the pressure of hydrogen ($P_{H/M=0.25}$) when

10 occluding hydrogen of 25 %, this value is calculated by the following formula.

$$SF = \ln (P_{H/M=0.75} / P_{H/M=0.25})$$

BRIEF DESCRIPTION OF THE DRAWINGS

The object and features of the present invention

15 will become more readily apparent from the following detailed description of the preferred embodiments taken in conjunction with the accompanying drawings in which:

Fig. 1 is a graph showing a relation between hydrogen pressure and hydrogen concentration in alloy

20 obtained when releasing hydrogen at a given temperature after compressed gas is sufficiently occluded in a hydrogen-occlusion-alloy;

Fig. 2 is a sketch cross-sectional drawing of a hydrogen-occlusion-alloy powder obtained according to the

25 present invention;

Fig. 3 is a cross-sectional view showing a structure in which a sponge-like nickel porous body is filled with the alloy powder according to the present invention;

Fig. 4 is a sketch cross-sectional drawing of the hydrogen-occlusion-alloy powder without both acid and alkali treatments;

Fig. 5 is a schematic drawing showing the structure of the storage battery of this invention;

Fig. 6 is a graph showing a relation between SF-value of alloys and charge-discharge cycle of batteries in which there are two types of alloys, namely, one type is treated with both acid and alkali according to the present invention and another type is not treated conventionally;

Fig. 7 is a graph showing a relation between the charge-discharge cycle and temperatures at which electrodes are treated with alkali;

Fig. 8 is a graph showing a relation between the charge-discharge cycle and immersion time at which electrodes are treated with alkali;

Fig. 9 is a graph showing a relation between types of separators and degrees of self-discharge; and

Fig. 10 is a graph showing a relation between contents of Manganese in alloys and degrees of self-discharge during preservation.

DETAILED DESCRIPTION OF THE INVENTION

Reffering to Figs. 2 to 6, one embodiment of the
present invention will be described hereinbelow. Misch
metal (Mm), nickel (Ni), cobalt (Co), aluminum (Al), and
manganese (Mn) are mixed in the ratio of the number of
atoms as follows:

1 : 3.5 : 0.8 : 0.3 : 0.4 respectively. The misch metal is
composed of mainly about 40 wt % of cerium, about 30 wt %
of lanthanium, and about 13 wt % of neodymium. The mixture
is melted by using a high-frequency furnace in the
atomosphere of inert gas. The mixture is transferred to a
container having a cooling apparatus while stirring, and
then, the mixture is rapidly cooled. The resulting alloy
is roughly crushed with a mechaniacal means. After this,
the alloy is heated to 1050 °C in the atomosphere of argon
gas and is held at 1050 °C for 3 hours, so that a
hydrogen-occlusion-alloy is obtained whose SF-value is 2.5
or below. Next, the alloy is crushed again to fine powder
whose diameter is 37 um or below. The powder is immersed
in a dilute nitric acid (1N) for a few minutes, and then,
is immersed in a KOH aqueous solution (7N) at 80 °C for 30m
minutes. By washing with water and drying, the alloy
powder 4 having numerous irregularities in the vicivity of
the surface layer whose depth is of approximately 0.01 um
is obtained. Fig. 2 shows a sketch cross-sectional drawing
of the hydrogen-occlusion-alloy powder obtained by the

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above-mentioned operation. In Fig. 2, numeral 1 denotes a portion having a high cristallinity in the powder. On the other hand, numeral 2 denotes a portion having a poor cristallinity where the alloy does not be composed by the above-mentioned compounding ratio when analyzing in detail. Numeral 3 denotes the surface layer of the alloy powder. A portion of (A) of the surface layer is enlarged and is shown in the circle. Not concerning the present invention, the mixture is melted in the high-frequency furnace which mixture composition is equal to that of the above-mentioned mixture of this invention, and then, is cooled as it is, namely, slow coolings. After this, the resulting alloy is mechanically crushed so as to make powder having a diameter of 37 μm or below. Fig. 4 shows a sketch cross-sectional drawing of the resulting powder. The meaning of the numeral in Fig. 4 is the same in Fig. 2. In this case, this alloy powder 4 is liable to separation due to the difference of the specific gravity of each element, and has many portion where cristallinity is poor. Comparing Fig. 4 with Fig. 2, the alloy in Fig. 2 differs largely from the all in Fig. 4 in that the alloy in Fig. 2 has a higher cristallinity and more numerous irregularities on the surface layer. The cristallinity of the alloy corresponds to the flatness of equilibrium pressure of hydrogen; namely SF-value, which can be obtained when releasing

hydrogen as shown in Fig. 1. Therefore, the cristallinity is generally expressed by SF-value. The smaller the SF-value, the higher the cristallinity even if the material is the same. The SF-value of the alloy in Fig. 4 is 2.7 to
5   3.4 whereas the SF-value of the alloy in Fig. 2 is 1.5 to 2.5.

A sponge-like nickel porous body that porosity is approximately 93 %, thickness is approximately 0.8 mm, and mean spherical space diameter is 400 μm is filled with a
10 paste-like mixture of the powder 4 of hydrogen-occlusion-alloy of this embodiment and a 5 wt % aqueous solution of a polyvinyl alcohol, and is dried. The obtained body is pressed, and then is cut, so that the resulting electrode is 0.5 mm thick, 39 mm wide, and 80 mm
15 long, and has a capacitance capable of charge and discharge of 1600 mAh. Fig. 3 shows a rough cross-sectional view of this electrode 10. In Fig. 3, numeral 4 denotes alloy powder, numeral 5 denotes a framework of the sponge-like nickel porous body, and numeral 6 denotes a space portion.
20   The battery system in the present invention is shown in Fig. 5. The battery comprises a casing, a negative electrode 10, a positive electrode 11, a separator 12, an electrolyte, a separator means, a sealing plate, a positive lead, a safety valve, a positive terminal, an insulator,
25 and an insulating gasket. The negative electrods 10, the

separator 12, and the positive electrode 11 are important
in this invention. Four sheets comprising the separator 30
sandwiched between the positive electrode 11 and the
negative electrode 10, and the separator means are wound in
the form of a roll. The electrolyte is mainly immersed
into the separator 12. Even if the electrolyte is not
described in the battery system, the electrolyte of a
conventional KOH aqueous solution is used in the battery
system hereinafter. A cylindrical sealed storage battery
of AA size is constructed by the resulting electrode 10, a
conventional nickel positive electrode 11 of foaming metal
type, an electrolyte, and a separator 12 of a nonwoven
fabric of a polypropylene introducing sulfonic acid group
and has the capacitance of approximately 1000 mAh. The
cycle test of charge and discharge at 20°C has been carried
out. Charge is carried out at 100 mA for 15 hours,
discharge is carried out at 200 mA to 1.0 V/cell, and
life-time is determined by the point where the capacitance
decreases to 80% of the initial capacitance.

Hydrogen-occlusion-alloys of this embodiment are ten
times made on an experimental basis, and alloys having
following SF-value are selected, i.e. 1.5, 2.0, 2.3 and
2.48. On the other hand, alloys are also made, but these
alloys are different from the above-mentioned alloys only
in that these alloys are conventionally cooled as it is,

namely, slow cooling. In the case of the later method, the
alloys take SF-value 2.3 to 3.4, and alloys having
following SF-value are selected, i.e. 2.52, 3.0 and 3.36.
Fig. 6 shows the result of the cycle test. In Fig. 6, the
5   samples (A') to (D') are obtained without acid and alkali
treatment, and each point in Fig. 6 is the average of
measurements of five storage batteries. SF-value is
plotted as abscissa against charge-discharge cycle as
ordinate in this figure. The contents of the comparison
10 samples, i.e. (B) to (D) and (B') to (D'), as well as (A)
and (A') will be described hereinbelow.

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Battery	(A) (A')	(B) (B')	(C) (C')	(D) (D')
Material of Alloy	$Mm\ Ni_{3.5}Co_{0.8}Al_{0.3}Mn_{0.4}$	$Mm\ Ni_{3.5}Co_{0.8}Al_{0.3}Mx_{0.4}$ or $Mm\ Ni_{3.5}Co_{0.8}Mn_{0.4}Mx_{0.3}$ in which Mx: Cu, Cr, or Fe	$Mm_{0.9}My_{0.1}Co_{0.8}Al_{0.3}Mn_{0.4}$ in which My: Ca, Ti or Zr	$Mm\ Ni_{4.3}Al_{0.3}Mn_{0.4}$
	(A'): no acid and alkali treatment	(B'): no acid and alkali treatment	(C'): no acid and alkali treatment	(D'): no acid and alkali treatment

As is apparent from this result, when the alloy powder 4 is
treated with both acid and alkali, there is a tendancy for
the cycling life-time property to be improved. Especially,
when alloys, whose SF-value are 2.5 or below, are treated
5 with both acid and alkali, the cycling life-time property
is extremely improved. However, in the case of alloys,
i.e. (D) or (D'), containing no cobalt, the degree of the
improvement in the above-mentioned property is small. From
these results, it seems that the acid and alkali treatments
10 mainly elute cobalt so that irregularity on the surface of
the alloy powder 4 is formed. Moreover, although the
combination of both acid and alkali treatments shows an
effect, the same result can be obtained even when acid
treatment or alkali treatment is carried out independently
15 for a given long time.

Therefore, in the electrode 10 where the negative
electrode material is the hydrogen-occlusion-alloy mainly
composed of misch metal and nickel and utilizing at least
cobalt as an element to be displaced, the sealed storage
20 battery having a long life-time can be obtained although
oxidation is drastic in this battery, by the method that
SF-value of the alloy material is 2.5 or below, cobalt is
eluted, and lanthanium series metals and nickel are
contained relatively at high ratio.

25 In this embodiment, alloy materials have been

described whose basic form is $MmNi_5$ of Ca_5Cu_5 type. However, alloy materials indicated by $MmNi_{4.7-5.3}$ of familiar type also have the crystal structure of $CaCu_5$ type, and show a similar tendency concerning the life-time property.

The powder is treated in the process of both acid and alkali treatments of this embodiment. However, in the state of pole plate where the sponge-like nickel porous body is filled with the paste-like mixture and then is dried, even if both acid and alkali treatments are carried out as well, the improvement of the cycling life-time has been recognized, and the same result has been obtained. The battery system is constructed by utilizing a silver oxide as the positive electrode 11 instead of the nickel oxide, and then the cycling life-time is examined. The cycling life-time is improved and the silver oxide as well as the nickel oxide is effectual, owing to the fact that SF-value of the alloy material of the negative electrode 10 is 2.3 or below, and irregularity on the surface is formed by both acid and alkali treatments. Therefore, as the positive electrode 11, metal oxides can be used which is utilized as the active material for the possitive electrode 11 of the alkaline storage battery.

Moreover, with the battery system being constructed by using the material of (A) and the three types of

separators 12, the amount of self-discharge is examined after the battery is fully charged and then leaves as it is at 45°C for a month. First separator 12 is made of a nonwoven fabric of a polyamide, second separator 12 is made of a nonwoven fabric of a polypropylene where surfactants are added so as to improve hydrophilic property, and third separator 12 is made of a nonwoven fabric of a polypropylene introducing sulfonic acid group. In the third separator 12, 55 to 60% of discharge capacitance is maintained in comparison with the discharge capacitance before the preservation whereas discharge capacitance is not practically detected in the first separator 12 and the second separator 12. It is effectual to use the separator 12 which is made of the nonwoven fabric of the polypropylene introducing sulfonic acid group in order to decrease the self-discharge.

Another embodiment of the present invention will be described hereinbelow. An alloy is melted by using a high-frequency furnace in the atmosphere of inert gas. The alloy has the composition of $Mm\ Ni_{3.5}\ Co_{0.8}\ Al_{0.3}\ Mn_{0.4}$ which composition is the same as that of the hydrogen-occlusion-alloy shown in the first embodiment. The alloy obtained by the method of the rapid cooling is heated in the atmosphere of argon gas, and then, without acid and alkali treatments, is crushed to make fine powder

whose diameter is 37 μm or below.

The resulting powder is mixed with a 5wt% aqueous solution of a polyvinyl alcohol so as to make a paste-like mixture. Then, a sponge-like nickel porous body is filled with the paste-like mixture, and is dried in the same manner as the first embodiment. After this, the electrode is immersed in a KoH aqueous solution (specific gravity is 1.30) for 12 hours. At this time, temperature is varied as follows: 30, 45, 50, 60, 80, and 100°C. Then, hydrogen-occlusion-electrodes as negative electrodes 10 are obtianed, by washing, drying, and pressing. The surface is magnified and observed by a microscope with the alloy powder 4 of the resulting hydrogen-occlusion-alloy being separated. As a result, irregularity in the vicinity of the surface is recognized as shown in Fig. 2, although there is a difference caused by the difference of the immersin temperaturs.

By cutting the resulting electrodes, the hydrogen-occlusion-electrodes having a length of 80 mm and a width of 39 mm are obtained. These electrodes 10 have a capacitance capable of charge and discharge of 1600 mAh or above. A cylindrical sealed battery of AA size is constructed by the combination of this electrode 10 and a conventional nickel positive electrode 11 of foaming metal tye, and this battery has a capacitance of approximately

1000 mAh. The cycle test of charge and discharge at 20°C has been carried out. The charge is carried out at 100 mA fo 15 hours, and the discharge is carried out at 200 mA to 1.0 V/cell. The battery constructing conditions are shown below, and the result of the cycle test of charge and discharge is shown in Fig. 7.

Battery	(E-1)	(E-2)	(E-3)	(E-4)	(E-5)	(E-6)	(E-7)
Immersion Temp.($^{\circ}$C)	no treat-ment	30	45	50	60	80	100

As is apparent from Fig. 7, in the case of the battery (E-1) constructed by the hydrogen-occlusion-electrode without immersing in the alkaline solution, the decrease of the capacitance is recognized when the number of cycles reach approximately 30. On the other hand, the cycling life-time increases with the increment of the immersion temperature, when the electrode is immersed. However, when immersed in the alkaline solution of 100°C, the battery shows unusual behavior. This is because the weight of the battery decreases. In order to guarantee the safety of the battery, the battery is provided with the safety valve which actuates when the pressure in the battery becomes 10 kg/cm^2 or above. Therefore, when inner pressure increases, the safety valve actuates to discharege the electrolyte out of the battery, so that the weight of the battery decreases. Namely, this is because inner pressure of the

battery arose on charging. Therefore, it is considered that when the electrode is treated at high temperatures, i.e. 100°C or above, the absorbing power of oxygen gas decreases and the amount of hydrogen to be occluded
5 electrochemically decreases, so that the pressure in the battery arises.

On the other hand, the relationship between the cycling life-time and the immersion time in a KOH aqueous solution (specific gravity is 1.3) is shown in Fig. 8. In
10 this figure, the cycling life-time is represented by the number of cycles of charge-discharge where the capacitance decreases to 80% of the initial capacitance. As is apparent from Fig. 8, the electrode can be immersed in the alkaline solution for 0.2 to 24 hours, when the battery is
15 obtained which has the property of the cycling life-time more than 200 cycles. Moreover, the electrode 10 can be immersed in the alkaline solution for 1.0 to 12 hours, when the battery is obtained which has the property of the cycling life-time more than 400 cycles.
20 As described above, even if the sponge-like nickel porous body is filled with the paste-like mixture of the alloy powder 4 and the 5 wt% aqueous solution of polyvinyl alcohl, is dried, and then, is immersed in the alkaline solution, numerous irregularities in the vicinity of the
25 surface of the alloy is formed so that this method also has

an effect on the property of the long life-time of the battery. It has a good effect on the electrode 10 that the alkaline solution is held at 50 to 100°C and is maintained for 0.2 to 24 hours. More preferably, it has a better

5 effect that the alkaline solution is held at 50 to 80°C and is maintained for 1 to 12 hours. Although in this embodiment, the alkaline solution with a specific gravity of 1.3 is applied, experiments are additionally made in the same manner using the alkaline solutions with a specific

10 gravity of 1.05 to 1.45. From the result of the experiments, since alkaline solution with a small specific gravity has a few effects, it is necessary for the electrode to be immersed in the alkaline solution for a long time in this case. Therefore, the alkaline solution

15 with a specific gravity of 1.1 or above has a sufficient effect on the electrode 10.

The other embodiment of the present invention will be described hereinbelow. This embodiment relates the battery system which is capable of the decrease of the

20 self-discharge. The alloy to be utilized as the negative electrode 10 is produced in the same manner as first embodiment. The composition of the alloy is represented as following formula.

$$Mm\ Ni_{3.95-x}\ Mn_x\ Al_{0.3}\ Co_{0.75}.$$
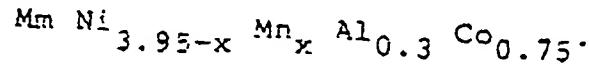
25 In this case, the amount of Ni and Mn is varied, namely,

value of X is changed as follows: 0, 0.2, 0.3, 0.4, 0.6, and 0.8. As a result, six kinds of alloys whose compositions are different are obtained. These six kinds of alloys are milled with a ball mill so as to make powder having a diameter of 37 µm or below. After this, in the same manner as second embodiment, the sponge-like nickel body is filled with the paste-like mixture of the alloy powder 4 and the 5 wt% aqueous solution of the polyvinyl alcohol, is dried, and then, the resulting material is immersed in the KOH aqueous solution with a specific gravity of 1.3 at 80 °C for 12 hours, is washed with water, is dried, and then, is pressed so that the negative electrode 10 is obtained.

In this case, three kinds of separators are utilized; that is, first separator 12 is made of the nonwoven fabric of polyamide, second separator 12 is made of the nonwoven fabric of the polypropylene where surfactants are added so as to improve hydrophilic property, and third separator 12 is the nonwoven fabric of the polypropylene introducing sulfanic acid group.

Although various methods for introducing sulfonic acid group are contrived, the following method is adopted. The nonwoven fabric of the polypropylene is immersed in 20% solution of fuming sulfuric acid for a given period of time so as to introduce sulfonic acid group to the

polypropylene. After this, the fabric is immersed in various concentrations of sulfuric acid in order; that is, first step 90%, second step 60%, and third step 30%. Lastly, the residual sulfuric acid is removed by washing

5   with water, and then, the fabric is dried. The resulting fabric is used as the sulfonated separator. In this case, the amount of sulfonic acid gruop to be introduced can be varied by the method of varying the time for immersing in the fuming sulfuric acid. In this embodiment, the degree

10   of sulfonation is measured with the immersion time being varied from 10 to 90 minutes. From this result, N-value is destributed from 20 to 250. N-value means the number of monomers in the polypropylene to which one sulfonic acid group is introduced. The sealed nickel-hydrogen storage

15   batteries of AA size, i.e. (F-1) to (F-13), having a discharge capacitace of approximately 1000 mAh are assembled by combinig these separators 12, the six kinds of the hydrogen-occlusion-electrodes described above, and the conventonal nickel positive electrode 11 of foaming metal

20   type as shown in Table 1.

25

Table 1

Battery	Composition of Alloy	Separtor (N-value)
F-1	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	20
F-2	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	25
F-3	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	53
F-4	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	92
F-5	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	148
F-6	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	250
F-7	$Mm\ Ni_{3.95}\ Al_{0.3}\ Co_{0.75}$	92
F-8	$Mm\ Ni_{3.75}\ Mn_{0.2}\ Al_{0.3}\ Co_{0.75}$	92
F-9	$Mm\ Ni_{3.65}\ Mn_{0.3}\ Al_{0.3}\ Co_{0.75}$	92
F-10	$Mm\ Ni_{3.35}\ Mn_{0.6}\ Al_{0.3}\ Co_{0.75}$	92
F-11	$Mm\ Ni_{3.15}\ Mn_{0.8}\ Al_{0.3}\ Co_{0.75}$	92
F-12	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	Polyamide (Conventional ex.)
F-13	$Mm\ Ni_{3.55}\ Mn_{0.4}\ Al_{0.3}\ Co_{0.75}$	Polypropylene (Conventional ex.)

N-value means the number of monomers in the polypropylen to which one sulfonic acid group is introduced.

The self-discharge is measured as described below.
The charge is carried out at charging rate of 0.1 CmA to
150% relative to a nominal capacitance of 1000 mAh, and the
discharge is continued at 0.2 CmA until the voltage becomes

5   1.0 V at 20°C. Both the charge and discharge are repeated
twenty times on the same condition described above, and
then, the charge is carried out in the same manner as
described above. Next, the batteries are maintained at
45°C for a given period of time after charging. Then, the

10 discharge capacitance is measured in such a way that the
discharge is carried out at the discharging rate of 0.2 CmA
until the voltage becomes 1V at 20°C. From these results,
retention capacity is calculated by comparing the resulting
discharge capacitance with the discharge capacitance before

15 preservation. In Fig. 9, storage period is plotted as
abscissa against the retention capacity as ordinate
concerning (F-1) to (F-6), (F-12), and (F-13). As is
apparent from Fig. 9, when battery (F-12) applying the
fabric of the polyamide to the separator 12 and battery

20 (F-13) applying the fabric of the polypropylene where
surfactants are added are preserved at 45°C for 30 days,
the retention capacity becomes 0%, namely, the degree of
the self-discharge is 100%.

25

On the contrary, batteries (F-1) to (F-6) using separators where N-values are 20 to 250, show an excellent effect. Namely, even if batteries are maintained at 45°C for 30 days, the retention capacity is 55 to 60%. However,

5 when the battery is constructed by utilizing the separator 12 made of the fabric of the polypropylene (N-value = 20), short phenomenon arises between the positive electrode 11 and the negative electrode 10 in proportion of one to four.

This is because the increment of the sulfonic acid group

10 causes the strength of the separator 12 to decrease. Moreover, when the separator 12 made of the fabric of the polypropylene (N-value = 250 or above) is applied to the battery, the time for injecting the electrolyte on constructing the battery is increased and the cycling

15 life-time of the battery is decreased. This is because the amount of sulfonic acid groups become extremely smaller. As a result, it became clear that the optimal N-value is 20 to 250.

Fig. 10 shows that the property of the

20 self-discharge is varied, when the component of the alloys is varied with the degree of sulfonation being fixed. As is apparent from Fig. 10, although the retention capacity of the battery (F-7) utilizing alloy without containing Mn is superior to that of the batteries (F-12) and (F-13)

25 shown in Fig. 9, the retention capacity is 40% or below

when maintaining for 30 days. However, when x is 0.2 or above in the formula of alloy, the retention capacity is 40% or above after maintaining for 30 days. However, when x is 0.8 or above in the formula of alloy, equlibrium

5   dissocation pressure of the hydrogen-occlusion-alloy decreases and the discharge capacitance becomes small. As a result, it is difficult to designe of the battery having a high capacitance.

In this embodiment, the nonwoven fabric of the

10   polypropylene having the porosity of 65% is used. However, when the battery is constructed by utilizing the nonwoven fabric of the sulfonated polypropylene having the porosity of 70% or above, the strength of the separator 12 decreases and short phenomenon arises. On the other hand, when the

15   sulfonated polypropylene having the porosity of 40% or below as the separator 12 is used, the penetrating velocity of oxygen generated at the positive electrode 11 on overcharging through the separator 12 decreases, and the electrolyte into the separator 12 increases. Therefore,

20   the absorptivity of oxygen gas on the surface of the negative electrode 10 decreases so that the increment of the pressure in the battery or the leakage of the electrolyte arises. As a result, the porosity of 40 to 70% is suitable for the sulfonated separator.

25

Moreover, polypropylene resin is used as one example of a polyolefine resin in this embodiment. However, the same result can be obtained even if polyethylene resin is used. Sulfonation is carried out by fuming sulfuric acid
5 in this embodiment. However, the same result can be obtained by limiting the degree of sulfonation as described above, even if the other sulfonating agents such as heated concentrated sulfuric acid or sulfur trioxide are used. As a result, this technique can be widely used by limiting the
10 degree of sulfonation.

The above-described embodiments are just examples of the present invention, and therefore, it will be apparent for those skilled in the art that many modifications and variations may be made without departing from the spirit of
15 the present invention.

20

25

A sealed storage battery comprises a positive electrode (11) including a metallic oxide as an active material, a negative electrode (10) including hydrogen-occlusion-alloy powder (4) capable of charging and discharging electrochemically hydrogen as an active material, an alkaline electrolyte, and a separator (12) for absorbing and holding the alkaline electrolyte. The hydrogen-occlusion-alloy powder (4) has a crystal structure of $CaCu_5$ type, is provided with numerous irregularities on the surface thereof, and has SF-value of 2.5 or below, which SF-value represents a plateau characteristic of equilibrium pressure of hydrogen releasing. The numerous irregularities on the surface of the alloy powder (4) causes oxygen being generated from the positive electrode (11) to be eliminated promptly.

WHAT IS CLAIMED IS:

1.   A sealed storage battery comprising:

     (a) a positive electrode including a metallic oxide;

5   (b) a negative electrode including hydrogen-occlusion-alloy powder having a cristal structure of $CaCu_5$ type, being provided with numerous irregularities on a surface, and having SF-value of 2.5 or below, said SF-falue representing a plateau characteristic of

10 equilibrium pressure of hydrogen releasing;

     (c) an alkaline electrolyte; and

     (d) a separtor for separating said positive electrode from said negative electrode, and for absorbing and holding said alkaline electrolyte.

15

2.   A sealed storage battery as claimed in claim 1, wherein a composition of said hydrogen-occlusion-alloy powder is represented by a formula, M Nix M'(5-x), said M being a single element or combined elements selected from a

20 group of Mn, Ca, Zr and Ti, said M' being a single element or combined elements selected from a group of Co, Al, Mn, Cu, Cr and Fe, and a value of x being 3 or above.

3.   A sealed storage battery as claimed in claim 1,

25 wherein sid positive electrode is nickel oxide.

4.   A sealed storage battery as claimed in claim 1,
wherein said separator is made of a polyolefine resin
introducing a sulfonic acid group or its alkali salts.

5

5.   A sealed storage battery as claimed in claim 1,
wherein irregularity on a surface of said
hydrogen-occlusion-alloy powder is made by mechanical
grinding or eluting a part of alloy components into acid
10   solution or alkaline solution.

6.   A sealed storage battery comprising:
    (a) a positive electrode including a sintered nickel
electrode or a non-sintered nickel electrode made by a
15   metallic porous body being filled with nickel compounds or
a nickel oxide;
    (b) a negative electrode including a
hydrogen-occlusion-electrode made by an alloy having a
cristal structure of $CaCu_5$ type, being represented by a
20   formula, $Mm_{1-x} M_{1x} Ni_y M_{2z}$, having SF-value of 2.5 or
below, and having numerous irregularities on a surface
layer of a powder of said alloy, said SF-value representing
a plateau characteristic of equilibrium pressure of
hydrogen releasing;
25   (c) an alkaline electrolyte; and

(d) a separator for separating said positive electrode from said negative electrode, and for absorbing and holding said alkaline electrolyte, in said formula Mm being misch metal, M_1 being a single element or combined elements selected from a group of Ca, Ti, and Zr with which said misch metal is replaced, M_2 being a single element or combined elements selected from a group of Co, Al, Mn, Cu, Cr, and Fe with which a part of nickel is replaced, x. y. and z being restricted by $1 > x \geq 0$, $y > 3.0$, $z > 0$ and $4.7 \leq y+z \leq 5.3$, said SF-value representing a plateau characteristic of equilibrium pressure of hydrogen releasing being calculated by an equality i.e. SF-value = $\ln (P_{H/M} = 0.75 / P_{H/M} = 0.25)$.

7. A sealed storage battery as claimed in claims 6, wherein hydrogen-occlusion-alloy powder is represented by $Mm\ Ni_{3.95-x}\ Mn_x\ Al_{0.3}\ Co_{0.75}$, in which $0.8 \geq x \geq 0.2$.

8. A sealed storage battery as claimed in claim 6, wherein said separator is a porous body of a polyolefine resin introducing a sulfonic acid group or its alkali salts.

9. A sealed storage battery as claimed in claim 6, wherein said separator is made of a polyolefine resin

introducing a sulfonic acid group or its salts, and the
number of monomers of polyolefine to one sulfonic acid
group or its salts is limited from 20 to 250.

5   10.   A sealed storage battery as claimed in claim 6,
wherein said separator made of a polyolefine resin
introducing sulfonic acid group or its salts has a porosity
of 40 to 70%.

10   11.   A method for making an electrode of a sealed storage
battery comprising the steps of:
          forming a hydrogen-occlusion-electrode by a metallic
porous body being filled with hydrogen-occlusion-alloy
power; and
15   forming fine irregularities on a surface layer of
sid hydrogen-occlusion-alloy by immersing said
hydrogen-occlusion-electrode in an acid solution or an
akaline solution so as to elute a part of alloy components.

20   12.   A method for making an electrode of a sealed storage
battery as claimed in claim 11, wherein said alkaline
solution is a potassium hydroxide aqueous solution having a
specific gravity of 1.1 or above, temperature of said
solution is in the range from 45°C to 100°C, and said
25   immersion time is in the range from 0.2 hours to 24 hours.

13.   A method for making an electrode of a sealed storage battery as claimed in claim 12, wherein said temperature of said alkaline solution is in the range from 50°C to 80°C,

5   and said immersion time is in the range from 1.0 hour to 12 hours.

10

15

20

25

FIG. 1

FIG. 2

(A)

3

1

3

1

2

FIG. 3

FIG. 4

FIG. 5

SAFTY VALVE

POSITIVE LEAD

POSITIVE TERMINAL(+)

SEALING PLATE

INSULATING GASKET

INSULATOR

SEPARATOR MEANS

CASE(-)

INSULATOR

NEGATIVE ELECTRODE 10

POSITIVE ELECTRODE 11

SEPARATOR 12
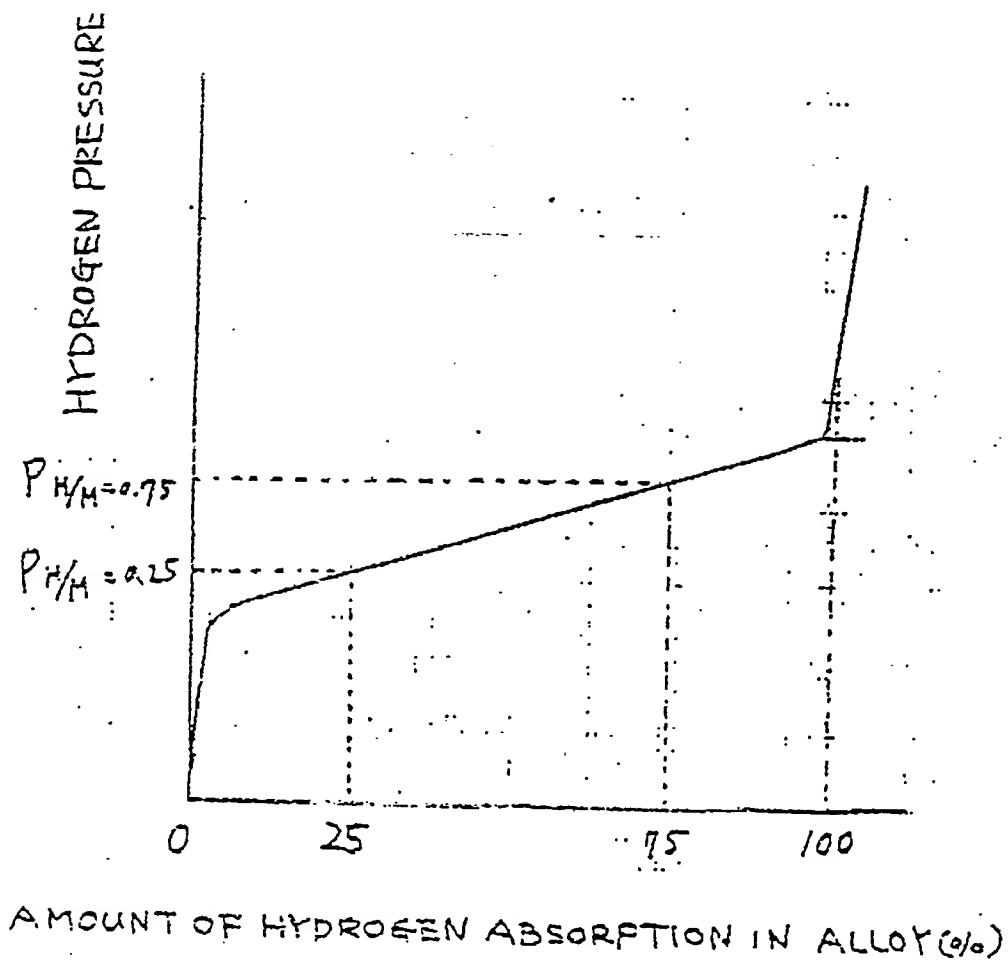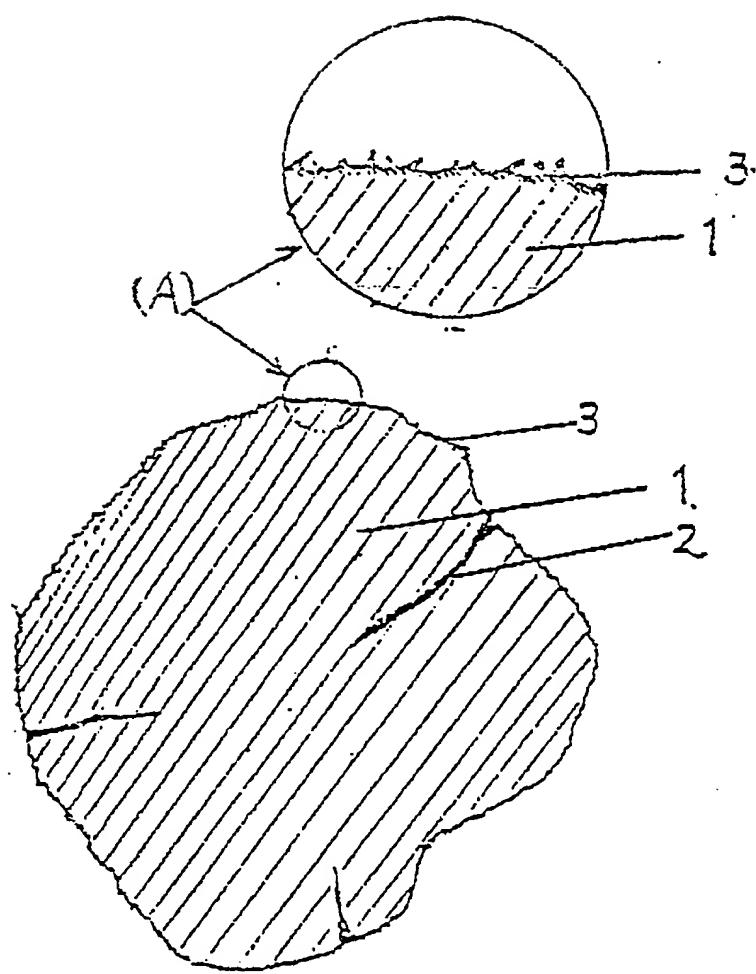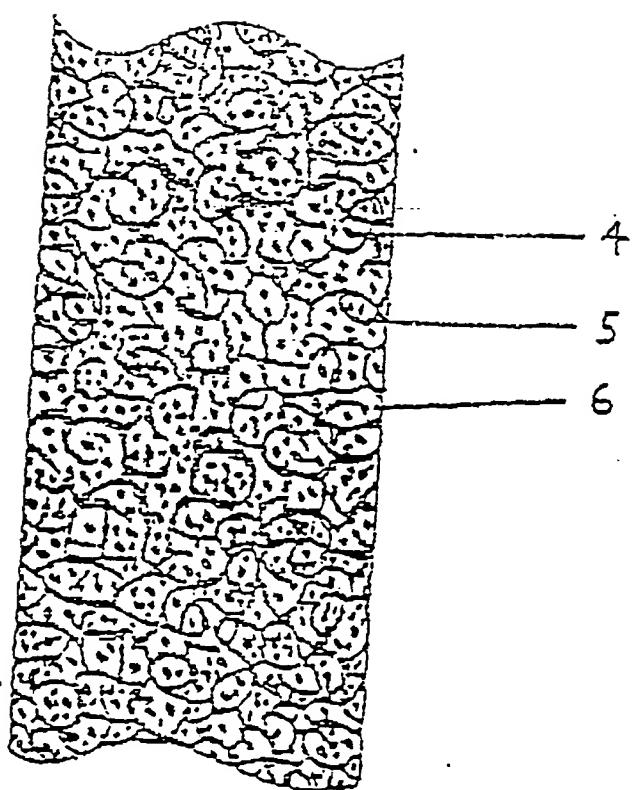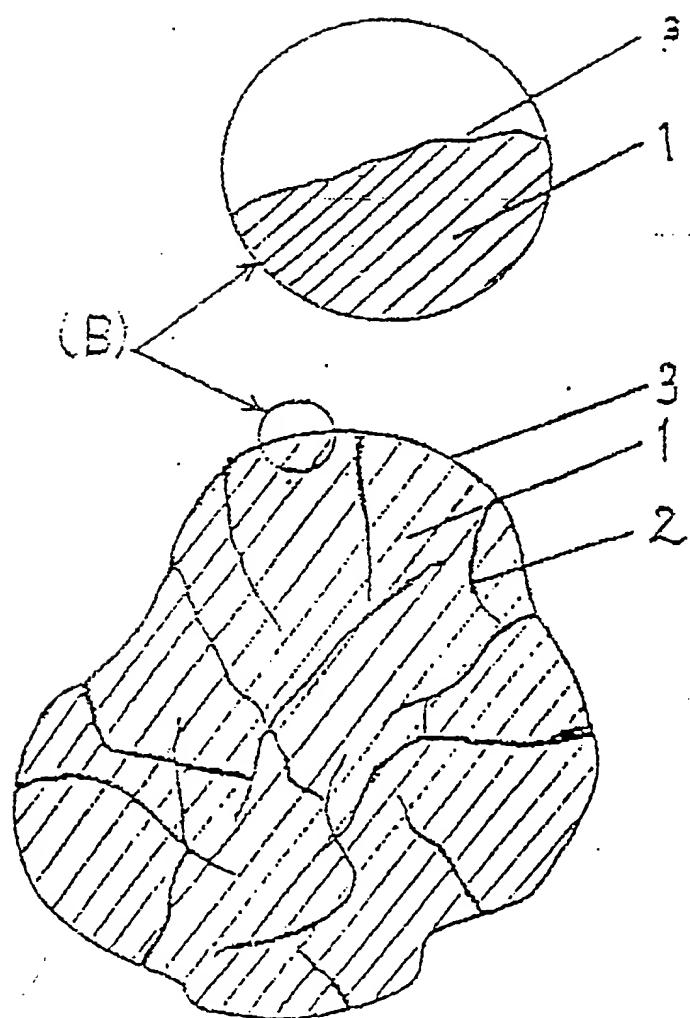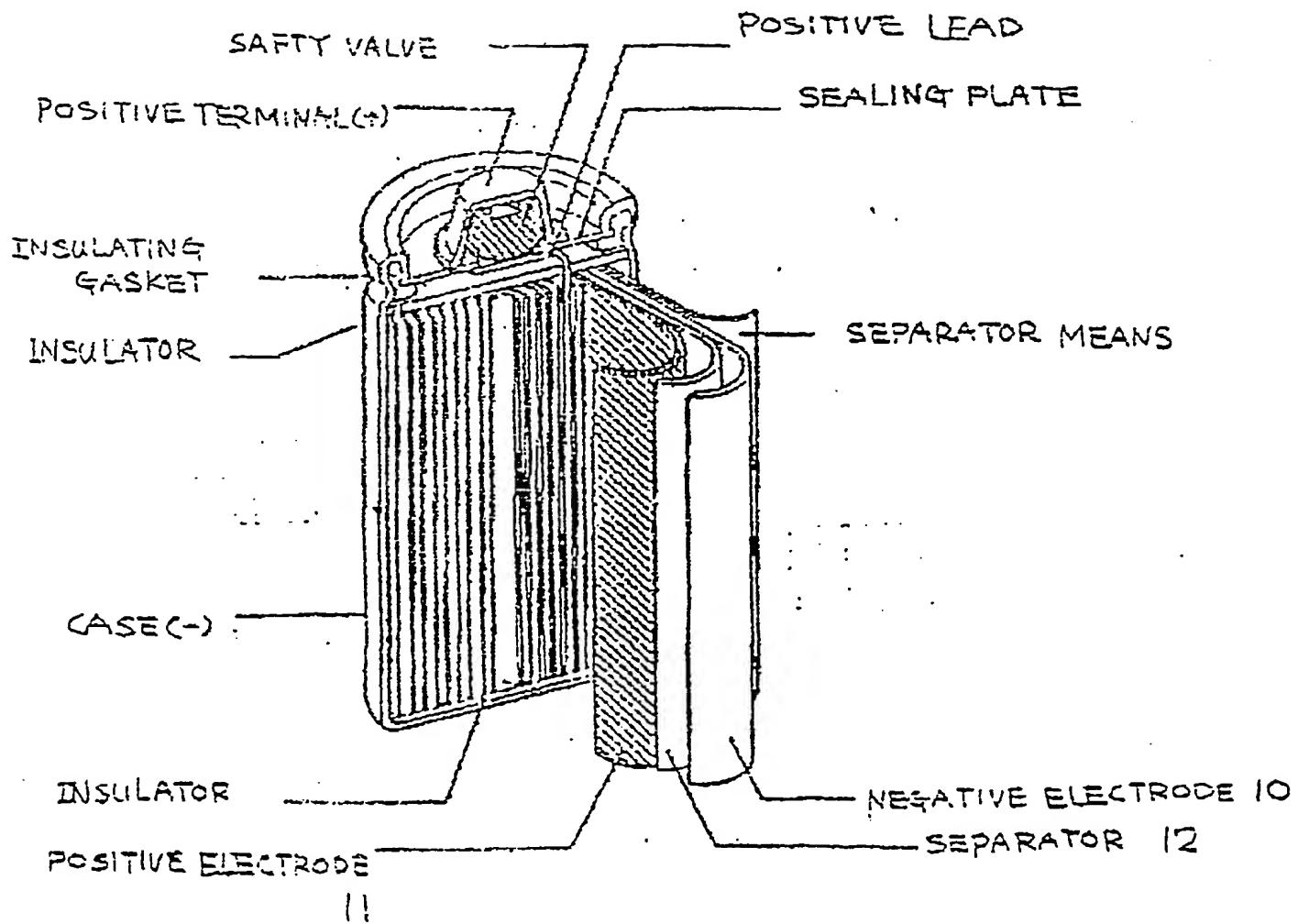
FIG. 6
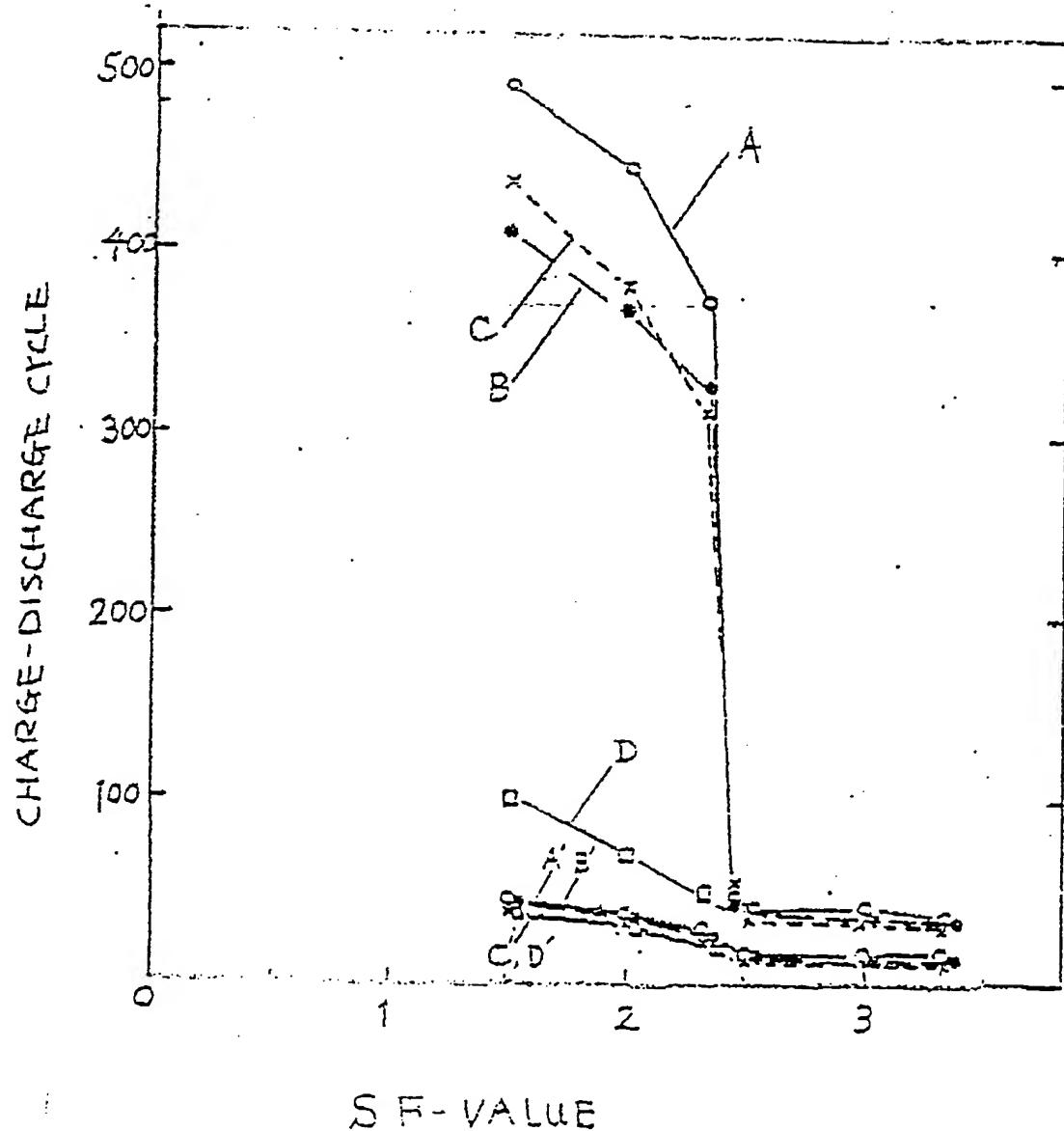
FIG. 7
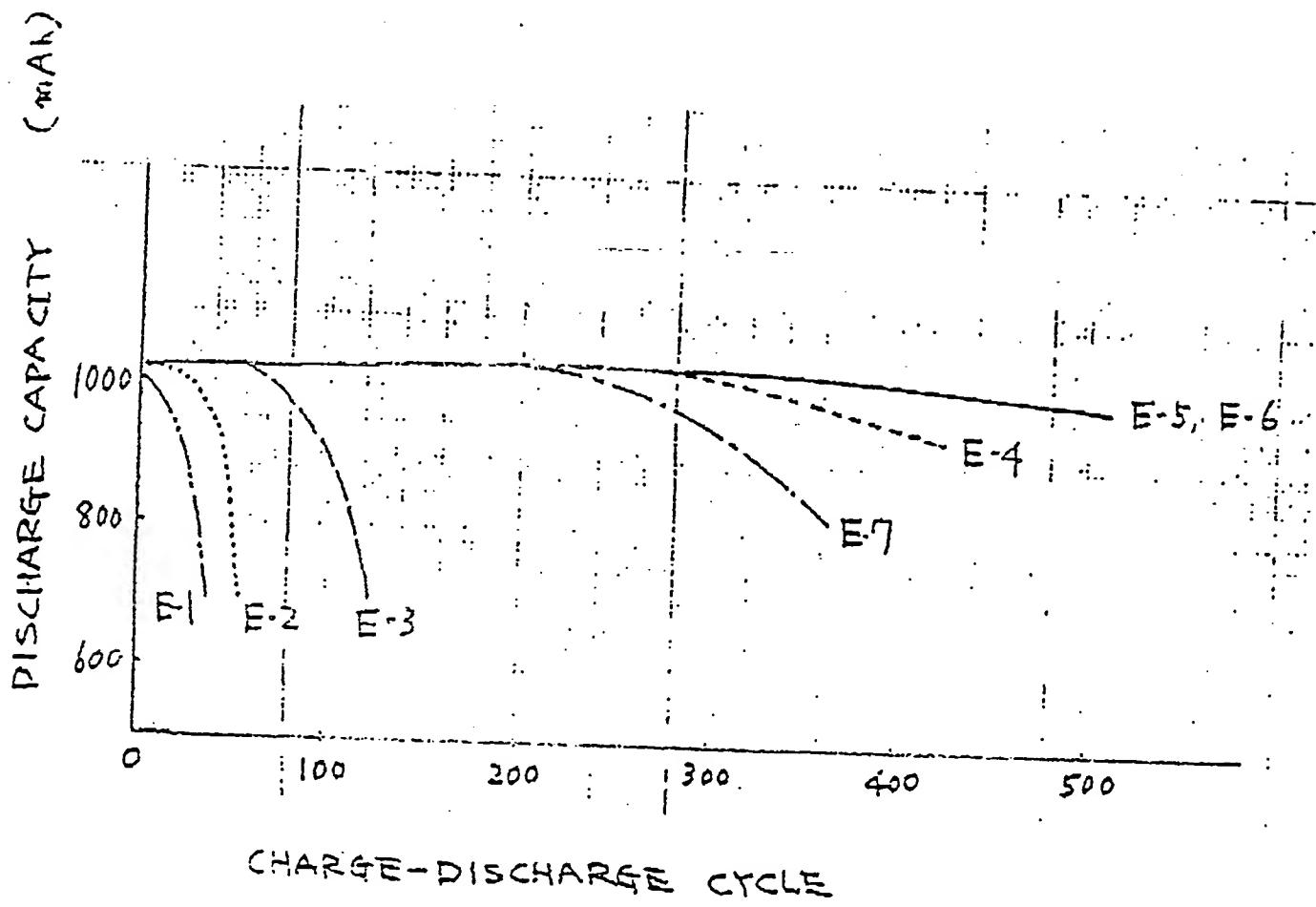
FIG. 8
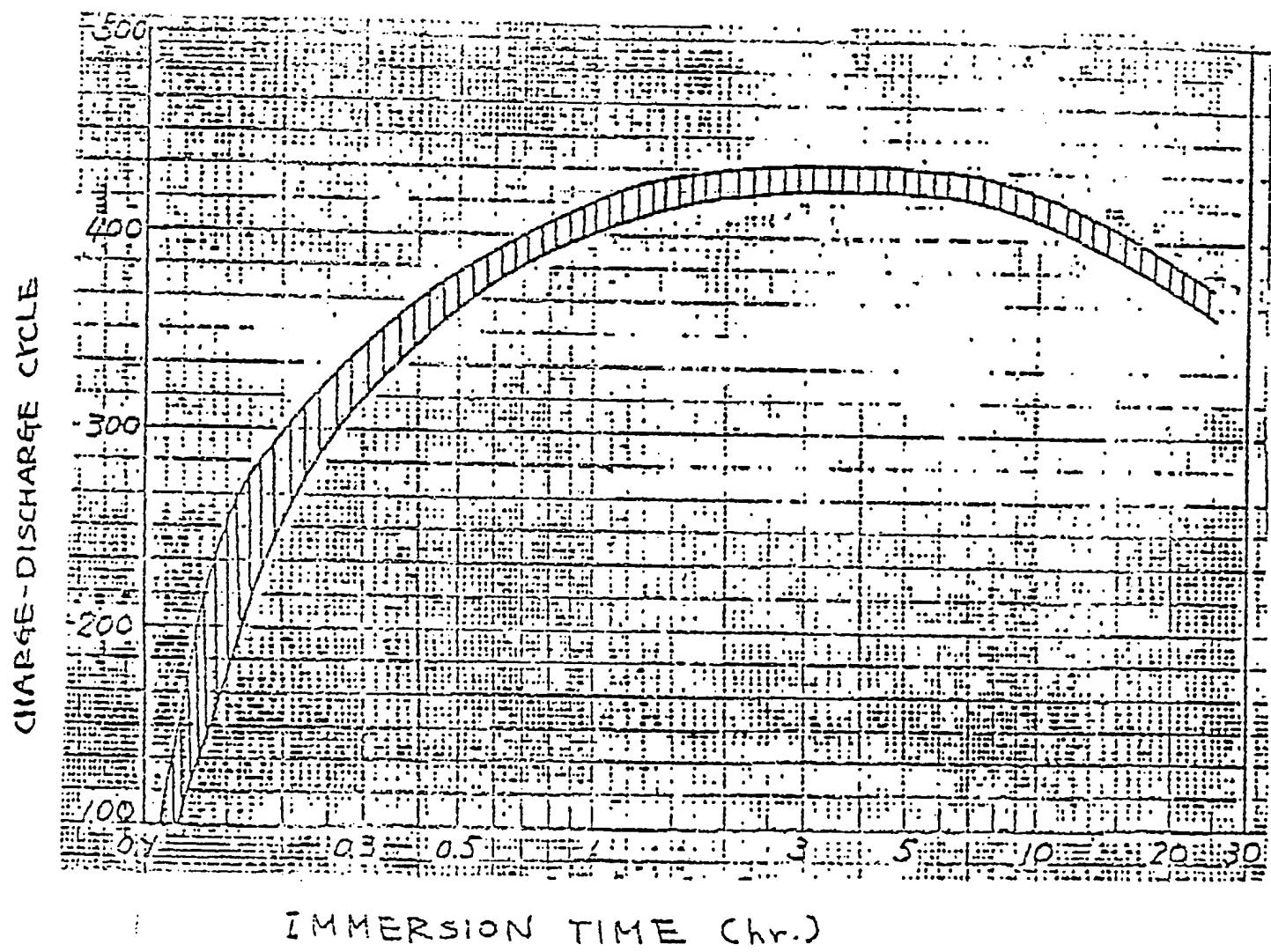
FIG. 9
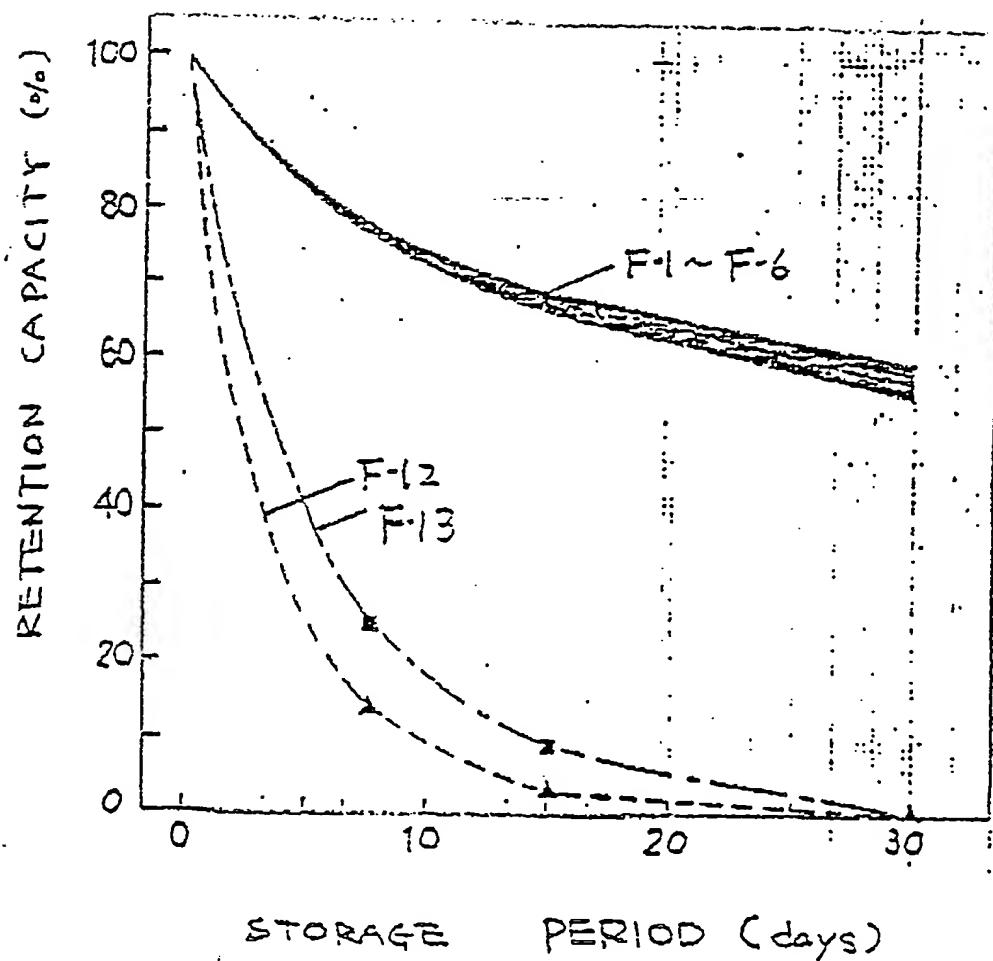
FIG. 10
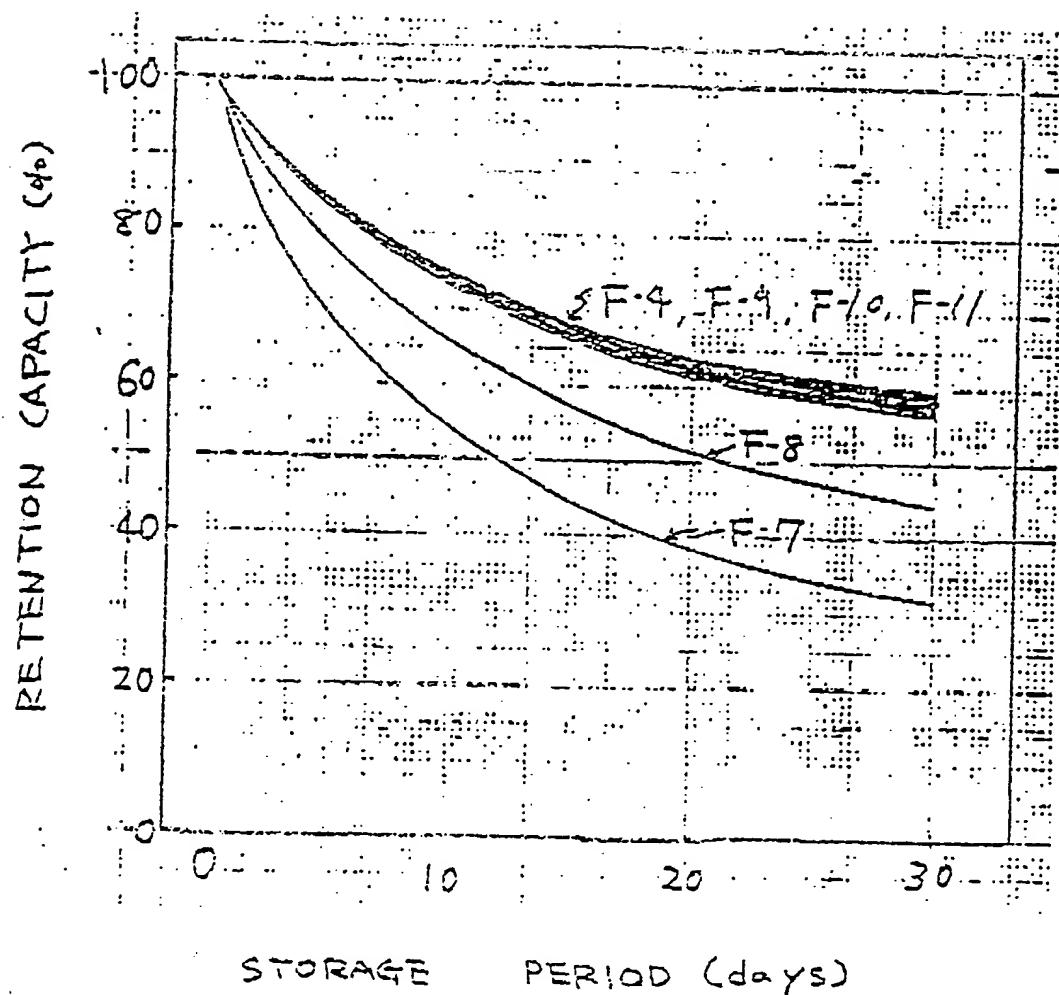
DOCUMENTS CONSIDERED TO BE RELEVANT

EP 87118066.7

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,A	CHEMICAL ABSTRACTS, vol. 106, no. 1, January 5, 1987, Columbus, Ohio, USA FURUKAWA, SANEHIRO et al. "Hydrogen absorbing anode" page 151, column 1, abstract-no. 7 556b & Jpn. Kokai Tokkyo Koho JP 61 168 871 --	1,6,7, 11	H 01 M 10/34 H 01 M 4/24 H 01 M 4/38 H 01 M 4/48
P,A	CHEMICAL ABSTRACTS, vol. 106, no. 1, January 5, 1987, Columbus, Ohio, USA FURUKAWA, SANEHIRO et al. "Metal-hydrogen alkaline battery" page 151, column 1, abstract-no. 7 557c & Jpn. Kokai Tokkyo Koho JP 61 168 870 --	1,6,7, 11	
A	EP - A2 - 0 170 519 (TOSHIBA) * Page 6, line 35 - page 7, line 16 * --	1,3,6,7	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)** H 01 M
D,A	GB - A - 2 162 994 (SANYO) * Page 1, line 59 - page 2, line 34 * ----	1,6,11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	15-03-1988	LUX